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STATISTICAL FINE STRUCTURE IN INHOMOGENEOUSLY BROADENED
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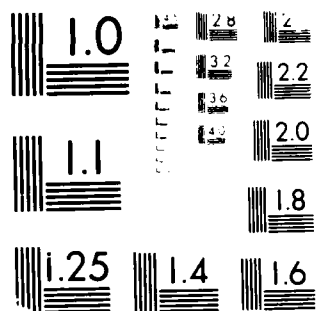
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in Solids

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W. E. Moerner and T. P. Carter

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STATISTICAL FINE STRUCTURE IN INHOMOGENEOUSLY BROADENED ABSORPTION LINES IN SOLIDS

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ABSTRACT

By using laser FM spectroscopy, we have observed statistical fine structure (SFS) in the inhomogeneously broadened zero-phonon $S_1 \leftarrow S_0$ (0-0) absorption of pentacene molecules in crystals of p-terphenyl at liquid helium temperatures. SFS results from variations in the spectral density of absorbers with optical wavelength due to statistics, illustrating that the inhomogeneous line profile is not a simple, smooth Gaussian function as has been previously assumed but rather contains significant fine structure. Theoretical analysis of the SFS spectra using autocorrelation techniques can be used to estimate the underlying value of the homogeneous linewidth. This new observation not only provides a novel way to study the statistics of inhomogeneous broadening, but it also allows estimation of the homogeneous width without requiring spectral hole-burning or coherent transient techniques.

INTRODUCTION

Inhomogeneous broadening is not only a universal feature of high-resolution laser spectroscopy of defects in solids¹, but it also appears in a fundamental way in other spectroscopies of impurity centers such as nmr, esr, and Mössbauer absorption. For zero-phonon transitions in crystals, the inhomogeneous profile (for a particular orientation or site) is composed of many narrow homogeneous absorption lines with a distribution of center frequencies caused by dislocations, point defects, or random internal electric fields and field gradients. Inhomogeneous broadening also occurs in amorphous hosts, where the center frequency distribution is caused by the large multiplicity of local environments.

Inhomogeneously broadened absorption lines are usually treated as smooth, Gaussian profiles. In recent work we have demonstrated the surprising fact that significant fine structure is a fundamental property of such lines². This structure is static and repeatable for a given probe volume; however, the structure changes completely for different probe volumes. Because we see no correlation between the frequency-dependent structure for different spatial positions, we feel that the source for SFS is statistical variations in the absorber spectral density with optical wavelength. For this reason, we call the effect "statistical fine structure" (SFS). We demonstrate that SFS can be detected in a *high* concentration sample by using a zero-background technique, laser frequency-modulation (FM) spectroscopy³. Information about the statistics of the centers and about the underlying homogeneous linewidth γ can be derived from the SFS spectra, without requiring spectral hole-burning⁴ or coherent transient techniques⁵.

EXPERIMENTAL

Measurements of SFS were performed on the inhomogeneously broadened optical absorption of pentacene molecules in p-terphenyl crystals at liquid helium temperatures. Samples were prepared from mixtures of sublimed pentacene and

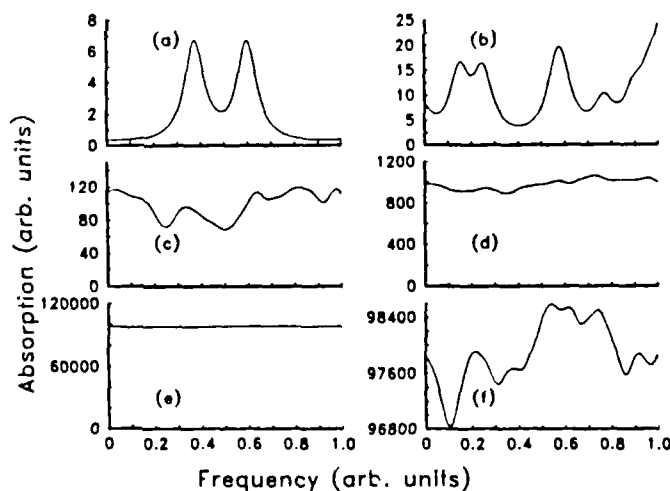
zone-refined p-terphenyl which were grown into single crystals using Bridgman techniques and cleaved into samples 200-300 μm in thickness. Concentrations ranged between 1×10^{-5} and 2×10^{-7} mole/mole, yielding low temperature optical densities at the peak of the O_1 site absorption⁶ between 0.01 and 0.15.

SCALING OF STATISTICAL FINE STRUCTURE

A simulation of expected lineshapes for varying numbers of centers helps in understanding the influence of concentration and sample configuration on the size of the SFS signals. We consider a fixed frequency interval $\Delta\nu$ within the inhomogeneous line that satisfies $\Gamma \gg \Delta\nu \gg \gamma$, where γ is the homogeneous linewidth (full width at half-maximum absorption, or FWIIM) and Γ is the FWIIM of the inhomogeneous line. We define the spectral density of absorbers in the probed volume $g(\nu)$ by requiring that $g(\nu)d\nu$ be the number of absorbers with center frequencies in $d\nu$ at ν . Then the number of centers per homogeneous linewidth is $N_H \equiv \int g(\nu)d\nu$ where the integral is performed over the spectral range γ , and the variations in $g(\nu)$ and thus in N_H with frequency form the underlying source of SFS. Let ΔN_H , \bar{N}_H and $\Delta\alpha$, $\bar{\alpha}$ signify the rms amplitude and mean value of N_H and α , respectively, over $\Delta\nu$.

We make the crucial assumption that the probability of a given center acquiring a particular center frequency in the range $\Delta\nu$ is constant. This is equivalent to assuming no "microsites" or special frequencies that are more probable than others within the interval. Figure 1 illustrates the variations in absorption coefficient that can then occur due to statistics alone.

Figure 1. Simulated absorption spectra with different values of \bar{N}_H . Traces (a) through (e) correspond to \bar{N}_H values of 0.2, 1, 10, 100 and 10,000, respectively. Trace (f) is an expanded trace of the same data as in (e).



To show how this figure was generated, let $I_\gamma(\nu) = (\gamma/2\pi)/[\nu^2 + (\gamma/2)^2]$ signify the assumed Lorentzian absorption of FWIIM γ for each center, then the full lineshape is

$$\alpha(\nu) = s \int_{-\infty}^{+\infty} g(x) I_\gamma(\nu - x) dx \equiv s g * I_\gamma(\nu), \quad (1)$$

where s is the integrated absorption strength per center and the asterisk signifies convolution. Figure 1(a) shows a possible lineshape if only two centers are in

Δv . Traces 1(b), (c), (d), and (e) show simulated lineshapes for $\bar{N}_H = 1, 10, 100$, and 10^4 . Clearly, $\bar{\alpha}$ is growing linearly with \bar{N}_H , while the relative fluctuations in absorption $\Delta\alpha/\bar{\alpha}$ are decreasing as $(\bar{N}_H)^{-1/2}$. Therefore, small \bar{N}_H samples ($\bar{N}_H < 10$, for example) would be expected to be optimal for the observation of SFS. However, detecting such a small number of centers in the presence of considerable background from the host matrix is quite difficult⁷.

Zero background techniques like FM spectroscopy provide a way around this problem, because the variable measured is $\Delta\alpha$ itself, which is growing as $(\bar{N}_H)^{1/2}$. Trace 1(f) demonstrates that SFS is still present even when \bar{N}_H is large.

FM SPECTROSCOPY DETECTION

Standard FM techniques³ employing an AD*P electro-optic phase modulator and a Si avalanche photodiode were used to phase-sensitively detect the SFS signal. Complete details of the apparatus will be presented elsewhere⁸. The crucial feature of the FM technique is that the detected signal varying as $\cos(2\pi\nu_m t)$, $F_1(\nu)$, is proportional to

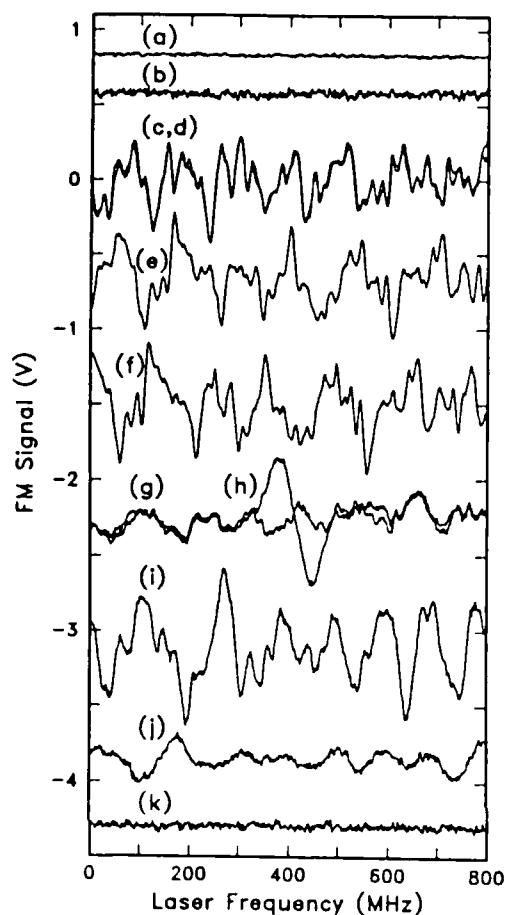
$$F_1(\nu) \sim -MP_0 e^{-\bar{\alpha}\ell} [\alpha(\nu + \nu_m) - \alpha(\nu - \nu_m)]\ell, \quad (2)$$

where ν is the laser frequency, ν_m is the rf modulation frequency, P_0 is the laser power on the sample, M is the modulation index, ℓ is the sample length, and $\bar{\alpha}$ is the background value of α . Thus the FM signal measures the difference in $\alpha\ell$ at the two sideband frequencies. (The component of the photocurrent varying as $\sin(2\pi\nu_m t)$, called $F_2(\nu)$, measures dispersion⁸.) $F_1(\nu)$ has two well-defined limits depending upon the ratio of ν_m to the linewidth of the spectral features³. When $\nu_m \gg \gamma$, $F_1(\nu)$ consists of two replicas of the Lorentzian line, one positive and one negative, separated by $2\nu_m$. In this regime $F_1(\nu)$ is maximal and independent of ν_m , and it is this regime that we use most often to detect SFS. Using the scaling results of the last section, the FM spectroscopy signal varies as $(\Delta\alpha)\ell = \sigma(\bar{N}_H)^{1/2}/\Lambda = \sigma(\rho\ell/\Lambda)^{1/2}$, where σ is the peak absorption cross section, Λ is the beam area, and the volume density per homogeneous linewidth is $\rho = \bar{N}_H/\Lambda\ell$. Therefore, $F_1(\nu)$ increases if the concentration of absorbers or the sample length increases, and increases for smaller laser spots. Further, centers with higher cross section lead to larger FM signals.

RESULTS AND DISCUSSION

Figure 2 shows FM spectra of SFS under varying conditions for pentacene in a single crystal of p-terphenyl. These spectra were acquired by repetitively scanning a R6G single-frequency dye laser (2.8 MHz linewidth) over the desired frequency range and averaging 64 scans. Unless stated otherwise, the laser was focused to a 20 μm diameter spot, the laser power was 3 μW , and the sample was immersed in superfluid helium at 1.4 K. The conditions for the various traces are summarized in the caption. Note in particular the following facts: the SFS spectrum for a single spot is highly reproducible (traces (c) and (d)), different spots on the sample show radically different SFS (trace (e)), larger beam areas show smaller SFS (trace (g)), persistent spectral holes can be burned (an unexpected result, trace (h)), and SFS disappears with increasing temperature due to the increase of γ above the fixed value of $\nu_m = 58.1$ MHz (traces (i), (j), and (k)). For the O_1 site of pentacene in p-terphenyl at 1.4 K, γ has been reported to be 7.8 ± 0.6 MHz⁹.

Figure 2. FM spectra (F_1) for a single crystal of pentacene in p-terphenyl. (a) No light on the detector. (b) $3 \mu\text{W}$ on the detector at a wavelength not in resonance with the O_1 site absorption. (c),(d) Spectra at 1.4 K near the peak of the O_1 absorption at 592.3 nm with a focused spot, where $\bar{N}_{II} \cong 5 \times 10^5$. (e) A new spot on the sample, same spectral range as (c). (f) Laser center frequency offset by 50 MHz from that for (e). (g) Large laser spot (0.75 mm diameter). (h) Persistent hole burned in the spectral range of trace (g) using 11 mW for 30 s (power broadened hole). (i) 1.4 K, focused spot. (j) 5.6 K, same location. (k) 7 K. The vertical scale is exact for (c) and (d); all the other traces have the same scale but are offset vertically for clarity. One volt corresponds to a change in $\alpha\mathcal{E}$ of 1.1×10^{-3} . The detection bandwidth was 0.1 Hz to 300 Hz and $\nu_m = 58.1 \text{ MHz}$ with $M = 0.16$. The frequency scale was calibrated by optically observing the rf sideband spacing.



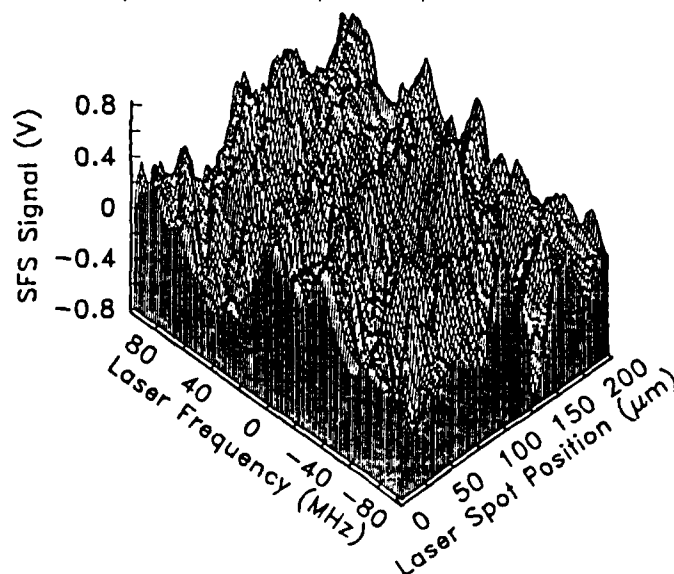
Results similar to those in Fig. 2 were obtained for the O_2 site where $\gamma = 7.3 \pm 0.5 \text{ MHz}$, but the O_3 and O_4 sites⁸ show smaller and broader SFS because γ is larger for O_3 and O_4 . In addition, as the laser frequency is moved away from the center of the inhomogeneous line, the amplitude of the SFS continuously decreases, as expected.

SFS provides a new window on inhomogeneously broadened lines with intrinsic detail and complexity. For example, recording of SFS spectra over a large fraction of the inhomogeneous profile may provide new information about the distribution of optical absorption energies available to the impurity centers. Furthermore, the rms amplitude of the SFS spectra should grow as $(\bar{N}_{II})^{1/2}$, and a measured dependence of $(\bar{N}_{II})^{0.54 \pm 0.05}$ has been observed experimentally (see Ref. 2). To check for the possibility of "microsites", the SFS spectra can be acquired as a function of position in the sample to see if the spectral structure at one position correlates with that at another position. Figure 3 shows a 3-dimensional plot over a 200 MHz range in frequency and a 200 μm range in laser spot position. No evidence for microsites or departures from the statistical source for the SFS have been observed in this system.

Estimates of γ can be extracted from the SFS spectra by exploiting the properties of autocorrelation functions. We consider the expected autocorrelation of the F_1 spectra, $\langle F_1 \star F_1 \rangle(\nu)$, in the limit $\nu_m \gg \gamma$. The result⁸ is

$$\langle F_1 \star F_1 \rangle(\nu) \propto -L_{2\nu}(\nu + 2\nu_m) + 2L_{2\nu}(\nu) - L_{2\nu}(\nu - 2\nu_m). \quad (3)$$

Figure 3. SFS structure versus laser spot position. A sequence of 100 spectra were obtained, moving the 20 μ m laser spot by 2 μ m after each spectrum, and the results plotted to show how the SFS structure changes as the laser spot is moved.



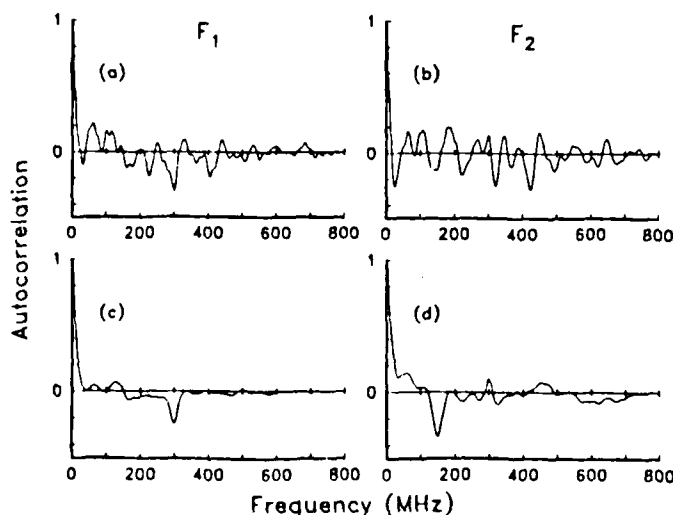
The expectation value of the autocorrelation of the FM signal has a FWHM equal to twice that for the underlying homogeneous absorption lines. Thus an estimate for γ can be derived from the FWHM or second derivative of $\langle F_1 \star F_1 \rangle(\nu)$ at the origin:

$$\gamma \approx \left[\frac{-2 \langle F_1 \star F_1 \rangle''(0)}{\langle F_1 \star F_1 \rangle(0)} \right]^{1/2}, \quad (4)$$

where the double prime signifies second derivative. (Eqn. (4) is also true for $\langle F_2 \star F_2 \rangle$, see Ref. 8).

To show how the expectation of the autocorrelation of the SFS signals approaches Eqn. (3), Figure 4 shows examples of measured single autocorrelation functions as well as the average of 10 autocorrelations for both F_1 and F_2 .

Figure 4. Autocorrelations of SFS spectra in F_1 and F_2 for the O_1 site with $\nu_m = 150$ MHz. Traces (a) and (b) show typical normalized autocorrelations of single SFS spectra. Traces (c) and (d) show the appearance of the peaks described by Eqn. (3) and by a similar equation⁸ for F_2 obtained by averaging only ten such spectra.



Long (4.8 GHz) laser scans are best for estimation of homogeneous widths because errors in the autocorrelation due to the limited spectral range of the data are minimized. For a single crystal sample with concentration 3×10^{-7} moles/mole, we find using Eqn. (4) that $\gamma = 7.9 \pm 0.8$ MHz for the O_i site at 1.4 K by analyzing the autocorrelations of six SFS spectra over a 4.8 GHz spectral range using $\nu_m = 150$ MHz. This value is consistent with the previously reported value ⁹ of 7.8 ± 0.6 MHz obtained using coherent transient techniques.

CONCLUSIONS

The central result of this work is that for an inhomogeneously broadened line, the spectral density of absorbers $g(\nu)$ is not a smooth Gaussian profile; rather, $g(\nu)$ contains significant statistical fine structure, even for high concentration samples. SFS should be a general feature of all inhomogeneously broadened lines in solids, and even in gases if measurements are performed on a time scale shorter than the collision time. We expect that SFS should be observable for color-centers, ions, and molecular vibrational modes in crystals as well as in amorphous media. We note that SFS imposes a fundamental limit on the detectability of shallow spectral features in inhomogeneous lines.

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